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COMMINUTION AND MECHANOCHEMICAL ACTIVATION IN OXIDE CERAMICS TECHNOLOGY (REVIEW)

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A classification of comminution equipment and conditions influencing the mechanical processing of raw-materials components for obtaining oxide ceramics is presented. It is recommended on the basis of an analysis of comminution (dispersion) and mechanochemical activation of alumina that impact (pressure) — shear (tube, vibratory, planetary, and so forth) mills be used. Mills with average power density 3 – 10 kW/kg are optimal for achieving high specific surface areas and high mechanochemical activation.

Key words: comminution, mechanochemical activation, impact-shear mill, power density.

Particle-size reduction (or comminution, dispersion) is an important step in the technology of oxide ceramics. The process itself is defined as mechanical crushing of solid particles into smaller particles without changing their aggregate state [1]. It can be used to obtain particles of a prescribed size and definite shape, increase the surface area, create defects, and conduct solid-phase reactions [1 – 6].

Dispersion of solids is a very energy intensive and very inefficient process — only about 5% of the energy consumed goes to particle-size reduction [2, 6]. This is why there is great interest in developing new designs for mills and in optimizing the process.

According to G. Heinicke [7], for dispersion in mills the mechanical load can be applied by means of compression (pressure), shear (rubbing), and impact by the milling body and collision. As a rule, a combination of these actions is observed in any given mill. All types of comminution setups can be conventionally divided into three basic groups [5, 6]:

1) impact mills (jet, hammer, and so forth), where the mechanical action is due to collisions between the particles themselves, with a plate or moving blades;

2) shearing setups (shafts, rollers, and so forth), where the action is due to the relative motion of surfaces between which the material being worked is placed;

3) mills where impact – pressure – shear (ball-tube, vibratory, planetary, and so on) work together and the ratio between the different actions varies within wide limits depending on the structural particulars and mill operating regime.

General features of these setups are the impulsive and local character of the actions.

Quite many factors affect the mechanical processing (MP) of a material in a mill. We shall examine the most important ones.

Mill Type. Ordinarily, mills are used for specific purposes [8, 9]. The comminution mechanism is decisive in one case and the particle-size distribution in another [1, 5].

Milling Body Material. The choice of material for the milling bodies is determined by the objective of the process [10]. Ordinarily, they include different special steels, corundum, carbides, nitrides, and so on [11]. In general, high-density milling bodies give better results because the applied force is larger. In addition, they must be denser and harder than the material being processed.

Milling Chamber Filling Factor. Mill chambers are never completely filled with milling bodies [1 – 3]. This is necessary in order to have enough room for the milling bodies and powder particles to able to move freely. Usually, the filling factor does not exceed 50% [11].

Milling Body to Powder Ratio. The ratio of milling bodies to powder or the charge is another important comminution parameter. It is the weight ratio of the milling bodies to the material load. A wide range of ratios has been used in different studies: from low values 1 : 1 to values reaching 220 : 1 [11].

Atmospheric Composition Effect. The components of the atmosphere can contaminate the product as well as give the desired effect. In the first case, the process is conducted

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in an inert medium (nitrogen, helium, and so on) [3, 11] and in the second case an atmosphere is created purposefully [12, 13].

Mill Rotation/Vibration Rate. The rotation/vibration speed of a mill, which depends on the type of mill, can have a large effect. Above a critical speed the balls are pressed against the walls of the milling chamber and will not exert an impact load on the powder particles. Below this critical speed the milling intensity will increase as the rotation/vibration rate increases. However, for higher rates the temperature of the milling chamber can reach high values [11].

Comminution Time. Many investigators are of the opinion that the processing time in a mill is the most important parameter of the process. This question will be examined in greater detail below.

Energy Delivered with Milling Bodies. This energy has a large effect on the efficiency of the process. It is not so much the total energy that is of decisive significance as the power of a single act [14]. This power is usually expressed through either the power density of a mill (for example, kW/kg of the material) or the acceleration of the milling bodies scaled to the acceleration of free fall (for tube mills this is 1*g*). H. Heegn has analyzed the particulars of the comminution processes in different types of mills and has presented formulas for calculating the mechanical energy delivered [6].

In a mill, when a mechanical pulse is delivered to a particle of the material being comminuted, energy is expended on imparting kinetic energy to the particle, heating as a result of friction, and creating a stress field on the surface of a particle [14]. The character and intensity of the stress field depend on the properties of the material being comminuted and on the characteristics of the comminution equipment. In addition, there are several relaxation paths [4, 15, 1 6]:

– mechanical energy is dissipated in the form of heat;

– when the stress field reaches a certain value of the energy, cracks can form and relaxation can occur with a new surface being formed;

– when relaxation occurs by means of plastic flow of a crystal (movement of point defects, dislocation motion, change of the concentration of defects and dislocations), the chemical properties of the material change;

– as stresses relax, destruction of crystal structure and amorphization, second-order phase transitions, occur.

In summary, when a material undergoes mechanical processing in a mill, not only comminution itself but also mechanochemical activation (MCA), which is accompanied by a change of the physical-chemical properties of the material, occurs. The actual process of mechanical processing of solid powdered materials can be conventionally divided into two stages [2, 3, 17, 18]:

1) comminution (dispersion) stage — this stage is characterized by an increase of the specific surface area, decrease of the region of coherent scattering (CSR) with a slight increase of microdeformations; association of mechanical energy occurs by means of an increase of the free energy of the surfaces formed;

2) mechanochemical activation stage — the specific surface area and the size of the crystallites remain constant, and the mechanical energy delivered accumulates in the form of the excess energy of crystal-lattice defects.

It was indicated above that the mechanical processing of a material is greatly affected by the character of the mechanical action, which is determined by the mill type. We shall illustrate this for the comminution of G-00 grade alumina. Photomicrographs obtained in a scanning microscope (Fig. 1) show very clearly the difference between the results of comminution and agree well with the data obtained by particle-size analysis [19].

The initial sample consists of large (of the order of 10 – 40 μm) aggregates, formed by monolithic blocks ranging in size from 5 to 15 μm. Processing alumina in comminution setups destroys aggregates and shears off the facets and asperities of the blocks. As a rule, the blocks themselves are not destroyed.

The most intense formation of a fine fraction is observed in mills with impact-shear loading (Fig. 1*b*, *c*, *d*, and *f*). In an impact-hammer mill (Fig. 1*e*) a fine fraction is formed, covers the larger particles, and prevents further comminution, damping the load applied by the comminuting organs.

Thus, for mechanical activation of powders it is necessary to use a mill in which the mechanical impulse from the milling body is delivered simultaneously with impact, pressure, and shear. This character of the load application gives a high degree of comminution and nearly spherical particles (this is especially important for extrusion ceramic technologies, because rheopexy of the molding pastes is eliminated [20]) as well as the tight contact required between the particles of the different ingredients for solid-phase interactions (a necessary condition for mechanochemical reactions to occur in activator mills). Examples of such mills are tube (ball, rod, and so on), vibratory (ball, roller-ring), and planetary mills.

As indicated above, the processing time of the material in a mill influences the efficiency of comminution and MCA. The following relation is suggested in [18, 21] for evaluating the efficiency Eff of the process:

$$\mathrm{Eff} = E_{\mathrm{st}} / E_{\mathrm{del}}, \qquad (1)$$

where E_{st} is the energy stored (associated) by the material and E_{del} is the energy delivered by the milling bodies.

Delivered Energy. This energy is proportional to the time and can be easily calculated using the equations presented in [6]. Here, only the energy which the milling bodies deliver directly during the action on the material being processes is taken into account. In the opinion of the authors, this approach makes it possible to evaluate the efficiency of mills more accurately on the basis of the character of the loading. However, if all energy which the mill obtains from the outside is used, then it will include the energy expended

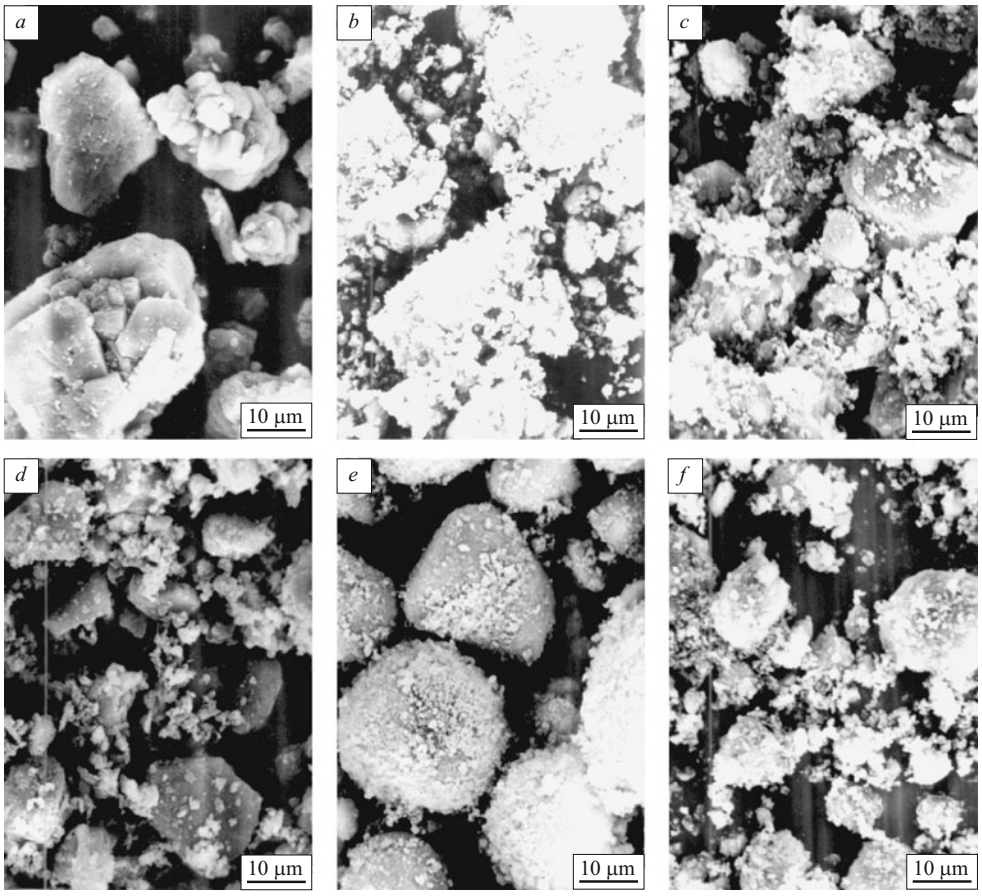

Fig. 1. Microstructure of alumina comminuted in different mills: *a*) initial sample; *b*) 30 h in a laboratory ball mill; *c*) 15 min in a VM-4 roller-ring mill; *d*) 15 min in an MTA vibratory ball mill; *e*) 10 min in a QC-114 impact-hammer mill; *f*) 10 min in an MG MOLM centrifugal planetary mill [20].

on putting the milling chamber or milling organs into motion, the losses in the driving mechanisms, and so on. It is obvious that all these energy losses are determined by the structural perfection of specific equipment and do not reflect the physical picture of the process.

Energy Stored during Activation. This is the excess energy of crystal- lattice deformations and includes the energy of stress relaxation during activation and the energy expended on chemical or polymorphic transformation [14, 22]. That is to say, stored energy is the energy which can be used subsequently in any chemical or physical transformation. This energy can be evaluated from the increase of the specific heat of the dissolution of the activated solid phase [17, 18] or from the decrease of the reaction energy of thermolysis [23].

Additives, first and foremost, surfactants, strongly influence the efficiency of comminution and MCA processes. Because they are adsorbed on the surface of the particles, they lower the surface energy and by penetrating into microcracks they increase the wedging force (the Rebinder effect). This results in the destruction of the solid-phase particles (comminution). Being sorbed by a newly formed surface the surfactant molecules prevent subsequent aggregation of the particles. Moreover, because of the adsorption-induced energy decrease the defect structures are stabilized not only on the surface but also in the interior volume of a crystal, which makes it possible to increase attainable degree of MCA [18, 19]. It must be underscored that the MCA enhancement in the presence of surfactants is due to not so much a change of the sizes of crystal-lattice defects $\Delta d/d$ as an increase of the extent (depth) of the strongly deformed layer [18].

Comminution in liquid media (usually water) also gives a positive effect. The liquid medium acts as a surfactant, promoting particle-size reduction and stabilization. However, a free liquid medium (water) will not work (and in many cases will be harmful) on increasing MCA, since the principal effect of a mechanical load decreases because the resistance of the medium is high [3]. For this reason, as a rule, dry comminution is used to obtain materials with a high MCA [2 – 5, 17 – 19, 23].

We shall now proceed directly to the question of determining the optimal comminution and MCA time. It is shown [17, 18] for mechanical processing of G-00 alumina in a VM-4 roller-ring vibratory mill that for dry comminution in

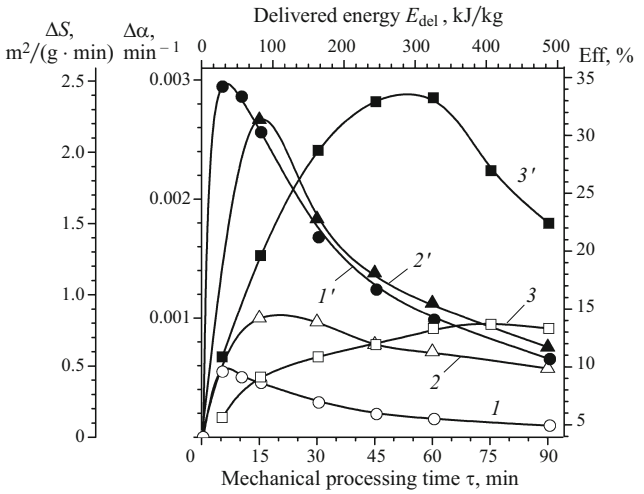

Fig. 2. Variation of the specific surface area ΔS (*1*, *1′*) and degree of hydration $\Delta\alpha$ (*2*, *2′*) of alumina as well as the energy efficiency Eff of the process (*3*, *3′*) versus the mechanical processing time and the delivered energy E_{del} in a vibratory mill: *1*, *2*, *3*) no additives; *1′*, *2′*, *3′*) in the presence of 5% surfactants.

the presence of polyvinyl alcohol (PVA) the attained specific surface area S_m (as determined by the BET method) increases from 12 to 60 m^2/g, and the degree of subsequent hydration of alumina α_{hydr} increases from 1.8 to 8.8 wt.%. To analyze the processes occurring during mechanical processing it is more convenient to construct the dependence not of the absolute values of S_m and α_{hydr} but rather their changes (Fig. 2). It is obvious that in this case the maxima of the curves will correspond to the optimal time. Here, two regularities can be identified:

1) the maxima of the curves of the variation of S_m and α_{hydr} versus the mechanical processing time with no surfactants occurs with more prolonged processing than in the presence of surfactants;

2) the maxima of the curves of the variation of S_m occur with shorter processing times than the maxima of the curves of the variation of α_{hydr} versus time.

In other words, the optimal mechanical processing time in the presence of surfactants is shorter, which only at the initial stages can be explained by an increase of the specific surface area. The subsequent growth of α_{hydr} is due to an increase of MCA (specifically, an increase of the density of defects in Al_2O_3 particles).

The equation (1) was used to evaluate the energy efficiency of mechanical processing. In the present case the stored energy E_{st} was evaluated according to the increase of the specific heat of dissolution of Al_2O_3 in sulfuric acid [18]. The increase of Eff at the initial stages of mechanical processing is due to the accumulation of energy predominately in the form of a newly formed surface. At subsequent stages of mechanical processing the energy is stored in the form of the excess energy of crystal-lattice defects, which, when released, increases the specific heat of dissolution in acid. More prolonged activation of the solid phase no longer gives such an energy accumulation effect, since the excessively deformed sections of the crystals relax directly during the MCA process (the energy relaxation paths were discussed above). Therefore, a large part of the delivered energy is expended directly during mechanical processing and is not stored. Large differences are observed in the position of the maximum of the curves of the rate of change of the degree of hydration $\Delta\alpha$ versus the mechanical processing time τ:

$$\Delta\alpha = (\alpha_{hydr} - \alpha_{hydr,\,\tau=0})/\tau,$$

where α_{hydr} is the degree of hydration of alumina at the running mechanical-processing time τ; $\alpha_{hydr,\,\tau=0}$ is the degree of hydration of the initial alumina at mechanical processing time $\tau = 0$.

These differences are explained by the fact that the hydration of Al_2O_3 is limited by diffusion through the product layer while for dissolution in acid such diffusion limitations are absent.

In summary, the optimal comminution (particle-size reduction) time corresponds to the maxima of the rate of change of the specific surface area ΔS as a function of the mechanical processing time in the mill

$$\Delta S = (\Delta S - S_{\tau=0})/\tau,$$

where ΔS is the rate of change of the specific surface area of the comminuted particles; S is the specific surface area at running mechanical-processing time τ; and, $S_{\tau=0}$ is the initial specific surface area at mechanical processing time $\tau = 0$.

Analysis of mechanical processing in different types of mills shows (see Table 1) that mills with high power density make it possible to obtain alumina with a high degree of MCA. However, the increase of MCA is not proportional to the increase of the power density of the mill. It occurs because relaxation processes occur directly in the mill, as discussed above. Here, a compromise solution must be found for technological problems.

High power density mills, such as planetary mills, make it possible to obtain solid materials with the highest degree of MCA in a short time. However, the energy efficiency of these mills is extremely low. In the opinion of the authors, for ceramic production it is better to use mills with average power density, for example, vibratory mills. Solid material with quite MCA is obtained in these mills, which makes it possible to use the stored energy efficiently at the subsequent stages of the production of articles, specifically, to optimize the molding properties [19, 20, 24], conduct the heat-treatment step under softer conditions [19, 2], and so on. Moreover, the energy efficiency and the optimal mechanical-processing time are very acceptable (see Table 1).

Similar results were obtained for MCA of hydrargillite [23].

TABLE 1. Characteristics of the Mechanical Processing of Alumina in Different Types of Mills

Mill type	Power density, kW/kg	Milling body acceleration	Surfactant additions (5%)*	Maximum admissible parameters					Optimal MCA time, min	Energy efficiency Eff, %
				Specific surface area S_m, m^2/g	CSR size D_m, nm	Microdeformation size e_m^*, %	Degree of hydration α_{hydr}^*, %	Degree of dissolution α_{dis}^*, %		
Ball-tube	0.02	1*g*	–	16	74.0	0.37	5.2	9.2	4000	32
			PVA	46	45.0	0.65	5.8	–	2000	50
			Paraffin	45	42.0	0.69	–	10.0	2000	–
Vibratory roller-ring	5.4	4.8*g*	–	19	47.5	0.82	6.1	10.4	80	12
			PVA	61	42.0	0.95	8.8	–	50	34
			Paraffin	59	39.5	0.99	–	15.7	50	–
Planetary	68.0	11.8*g*	–	16	46.0	0.84	6.4	10.8	5	0.1
			PVA	57	31.5	0.94	9.2	–	3	0.3
			Paraffin	54	31.0	1.02	–	16.1	3	–

* Content, wt.%.

CONCLUSIONS

In summary, it best to use the following for comminution (particle-size reduction) and MCA of the raw-materials components to obtain ceramic articles:

1) mills with impact (pressure) — shear loading, since they give nearly spherical particles with high dispersity and high specific surface area;

2) mills with average power density (3 – 10 kW/kg), since a quite high MCA is attained in them, which makes it possible to increase considerably the efficiency of the subsequent technological operations; the energy efficiency and the optimal comminution and MCA times are acceptable.

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